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TERNARY PHASE EQUILIBRIA IN TRANSITION METAL-BORON-CARBON-SILICON SYSTEMS

Part I. Related Binary Systems
Volume VII. Ti-B System

E. Rudy
St. Windisch

Aerojet-General Corporation

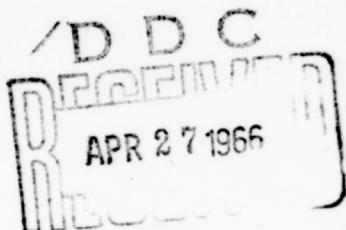
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TERNARY PHASE EQUILIBRIA IN TRANSITION METAL-BORON-CARBON-SILICON SYSTEMS.

Part I. Related Binary Systems.

Volume VII. Ti-B System.

⑯ Technical rept.,

⑯ ⑯

E. Rudy
St. Windisch.

⑯ AF/33(615)-1249

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FOREWORD

The work described in this report was carried out at the Materials Research Laboratory, Aerojet-General Corporation, Sacramento, California, under USAF Contract No. AF 33(615)-1249. The contract was initiated under Project No. 7350, Task No. 735001. The program is administered under the direction of the Air Force Materials Laboratory Research and Technology Division, with Captain R. A. Peterson and Lt. P. J. Marchiando acting as Project Engineers, and Dr. E. Rudy, Aerojet-General Corporation, as Principal Investigator. Professor Dr. Hans Nowotny, University of Vienna, served as consultant to the project.

The project, which includes the experimental and theoretical investigation of related binary and ternary systems in the system classes Me_1 - Me_2 -C, Me -B-C, Me_1 - Me_2 -B, Me -Si-B, and Me -Si-C, was initiated on 1 January 1964.

The phase diagram work was performed by E. Rudy and St. Windisch. Assisting in the investigations were: J. Pomodoro (preparation of sample material), T. Eckert (DTA-runs), J. Hoffman (metallographic preparations), and R. Cobb (X-ray exposures).

Chemical analysis of the alloys was performed under the supervision of Mr. W. E. Trahan, Quality Control Division of Aerojet-General Corporation. The authors wish to thank Mr. R. Cristoni for the preparation of the illustrations and Mrs. J. Weidner, who typed the report.

The manuscript of this report was released by the authors October 1965 for publication as an RTD Technical Report.

Other reports issued under USAF Contract Af 33(615)-1249 have included:

Part I. Related Binaries

- Volume I, Mo-C System
- Volume II, Ti-C and Zr-C Systems
- Volume III, Systems Mo-B and W-B
- Volume IV, Hf-C System
- Volume V, Ta-C System. Partial Investigations in the Systems V-C and Nb-C
- Volume VI, W-C System. Supplemental Information on the Mo-C System

Part II. Ternary Systems

- Volume I, Ta-Hf-C System
- Volume II, Ti-Ta-C System
- Volume III, Zr-Ta-C Systems
- Volume IV, Ti-Zr-C, Ti-Hf-C, and Zr-Hf-C Systems

FOREWORD (Cont'd)

Part III. Special Experimental Techniques

Volume I, High Temperature Differential Thermal
Analysis

Part IV. Thermochemical Calculations

Volume I, Thermodynamic Properties of Group IV,
V, and VI Transition Metal Carbides

This technical report has been reviewed and is approved.



W. G. RAMKE
Chief, Ceramics and Graphite Branch
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ABSTRACT

The binary system Ti-B, has been investigated by means of X-ray, metallographic, melting point, and differential thermoanalytical techniques, and a complete phase diagram for the system was established. The results of the present investigation are discussed and compared with previous findings.

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I. INTRODUCTION AND SUMMARY

A. INTRODUCTION

Among the intermediate phases formed between the refractory transition metals and boron, the diborides of the group IV metals titanium, zirconium, and hafnium, exhibit the highest degree of oxidation resistance. In view of these as well as other desirable properties, such as refractoriness, high stability, high heat conductivity, etc., considerable efforts have been made over the past few years to exploit these properties in structural parts for high temperature applications. Noticeable, the investigations by L. Kaufman and co-workers⁽¹⁾ have contributed much to our understanding of the principles governing the high temperature stability of this compound class and also have shed some light on the limiting factors in their high temperature application in corrosive gas environments.

Like the other interstitial type compounds, such as the carbides and nitrides of the refractory transition metals, the borides are hard and brittle, and hence susceptible to mechanical or thermal shock loads. The possibilities in applying them as single-phased materials are therefore very limited. Recent efforts⁽²⁻⁷⁾ to eliminate these difficulties by combining the beneficial properties of the borides in suitable composite systems were of limited success only, since unpredictable reactions between the components posed serious problems.

Despite the interest in the borides, comparatively little is known about the phase-relationships in ternary and higher metal-boron systems. In view of the growing demand for phase diagram data in this important system class, one task of the present program was devoted towards the initiation of systematic studies of the phase relationships in multicomponent metal-boron

systems. Although the initial objective was restricted to selected ternary systems, certain inconsistencies with presently available binary system data became apparent in the course of the work; the investigation of selected binary metal-boron systems was therefore initiated as a subtask to the investigation of the ternaries in a latter part of the program.

The present report is the second in the series of documentary reports on binary metal-boron systems. Other binary systems which have been investigated, include Zr-B, Hf-B, V-B, Nb-B, Ta-B, Mo-B, and W-B. The last mentioned two systems already were reported previously⁽⁸⁾; the remaining group IV and V metal-boron systems will be the subject of follow-on reports.

B. SUMMARY

With the exception of Ti_2B , $TiB(B1)$, and Ti_2B_5 , all previously reported phases could be confirmed. Two stable intermediate phases, a peritectically decomposing monocarbide of orthorhombic crystal structure, and an extreme high-melting diboride with hexagonal symmetry, occur in this alloy system. Phase diagram details are summarized below.

1. The Titanium Phase

The pure metal melts at $1668 \pm 8^\circ C$; at the eutectic temperature $Ti + TiB$ ($1540 \pm 10^\circ C$) takes less than one (1) atomic percent boron into solid solution. Within the experimental error limits, the addition of boron has no effect on the α - β -transformation temperature of titanium ($880^\circ C$). The eutectic point β - $Ti + TiB$ is located at $1540^\circ C$ and at a boron concentration of 7 ± 1 atomic percent.

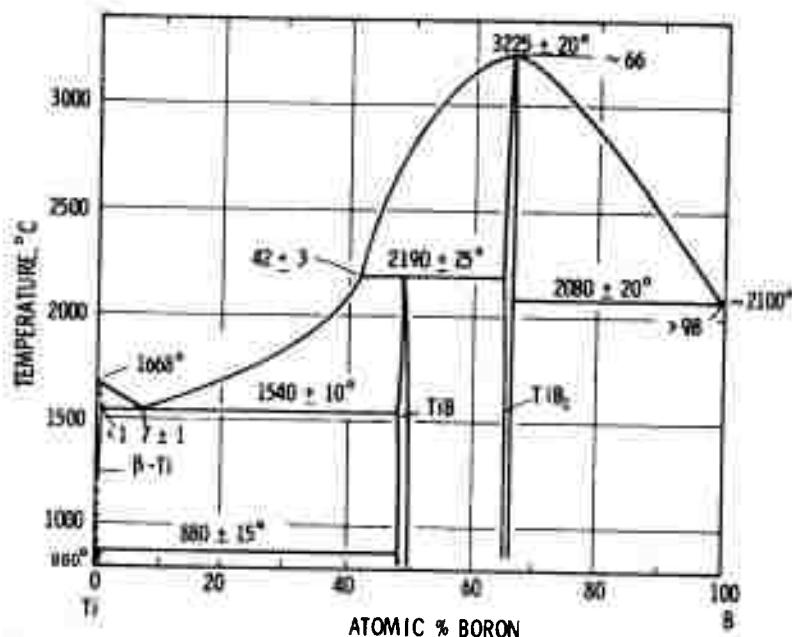
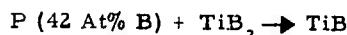


Figure 1. Constitution Diagram Titanium-Boron

2. Titanium Monoboride

Titanium monoboride, with an orthorhombic, B27 type, of structure ($a = 6.10 \text{ \AA}$; $b = 3.06 \text{ \AA}$; $c = 4.56 \text{ \AA}$), and a negligible range of homogeneity, is formed in a peritectic reaction at 2190°C from melt and diboride according to



The phase probably occurs at slightly understoichiometric ($\sim 1 \text{ At\%}$) compositions.

3. Titanium Diboride

Titanium diboride, isomorphous with the other

diborides of the group V and group VI transition metals, has an hexagonal, C32 type of structure, with $a = 3.032 \text{ \AA}$, and $b = 3.225 \text{ \AA}$. The phase, whose range of homogeneity is less than two atomic percent over the entire temperature range, melts congruently at $3225 \pm 20^\circ\text{C}$ at the stoichiometric composition. The diboride forms a eutectic equilibrium with boron ($\sim 98 \text{ At\% B}$, $2080 \pm 20^\circ\text{C}$).

Table 1. Isothermal Reactions in the System Titanium-Boron

Temperature °C	Reaction	Compositions of the Equilibrium Phases, At% B			Type of Reaction
3225	$L \rightarrow TiB_2$	66	66	--	Congruent Transfor- mation
2190	$L + TiB_2 \rightarrow TiB$	~42	65	~49	Peritectic Reaction
2100	$L \rightarrow B$	100	100	--	Melting Point of Boron
2080	$L \rightarrow TiB_2 + B$	98	66.6	>99	Eutectic Reaction
1668	$L \rightarrow \beta\text{-Ti}$	100	100	--	Melting Point of $\beta\text{-Ti}$
1540	$L \rightarrow \beta\text{-Ti} + TiB$	7	<1	49	Eutectic Reaction
880	$\beta\text{-Ti} + TiB_2 \rightarrow \alpha\text{-Ti}(?)$	<1	<1	--	Probably Peritectic Reaction
880	$\beta\text{-Ti} \rightarrow \alpha\text{-Ti}$	--	--	--	$\alpha\text{-}\beta$ -Transformation in Ti

II. LITERATURE REVIEW

Four compounds, Ti_2B , TiB , TiB_2 , and Ti_2B_5 , have been claimed to occur in this alloy system⁽³⁾, but only the phases TiB ($B2$) and TiB_2 appear as firmly established. The presently accepted phase diagram of the system, based mainly on investigations by A. E. Palty, H. Margolin, and J. P. Nielsen^(3, 9) is shown in Figure 2.

B. Post and W. Glaser⁽¹⁰⁾ observed the formation of a tetragonal compound Ti_2B , and derived parameters of $a = 6.11 \text{ \AA}$ and $c = 4.56 \text{ \AA}$ (Table 2). Apparently the same compound also had been prepared by A. E. Palty and co-workers⁽⁹⁾ and was said to be stable only within the temperature range from 1800 to 2200°C (Figure 4). According to their results, two tetragonal unit cells, $a = 6.10 \text{ \AA}$, $c = 4.53 \text{ \AA}$, or $a = 5.24 \text{ \AA}$, $c = 7.602 \text{ \AA}$, would fit the observed X-ray patterns. The occurrence of a superlattice of the hexagonal close packed titanium phase in titanium-boron alloys with boron concentrations between 9.1 to 44.4 At. % B ⁽¹¹⁾ was later claimed to have been a mixture of α -titanium and Ti_2B ^(9, 12). In discussing boride structures, B. Aronsson⁽¹⁵⁾ attributes earlier observations of a Ti_2B due to a false interpretation of the X-ray patterns, which actually referred to the monoboride.

Claims for a face-centered cubic ($B1$ or $B3$)⁽¹¹⁾ monoboride with a lattice parameter of $\sim 4.25 \text{ \AA}$ ^(10, 11, 14, 15, 19) were doubled by L. Brewer, et.al.⁽¹⁶⁾, saying, that their appearance was due to nitrogen (oxygen) and carbon contamination of the alloys. The true binary phase TiB , occurring at compositions close to stoichiometry, has orthorhombic symmetry⁽¹⁷⁾ (Table 2), with $a = 6.12 \text{ \AA}$, $b = 3.06 \text{ \AA}$, and $c = 4.56 \text{ \AA}$.

The extreme stable diboride has a hexagonal, C32-type of crystal structure (11, 18, 19) (Table 4). The existence of higher borides, a Ti_2B_5 with a crystal structure analogous to that of W_2B_5 ⁽¹⁰⁾, as well as a further phase TiB_{10} , observed by H. M. Greenhouse, et.al.⁽²⁰⁾, has not been confirmed in more recent work.

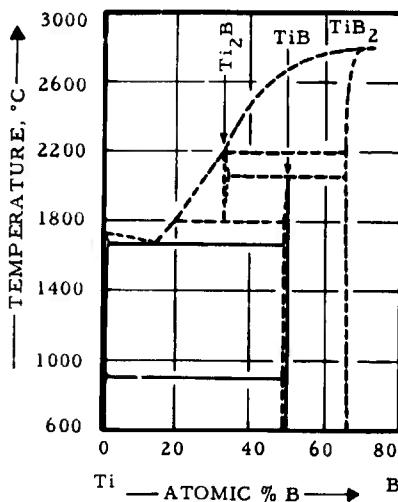


Figure 2. Phase Diagram Titanium-Boron.
(A.E. Palty, H. Margolin, and J.P. Nielsen, 1954)

The solid solubility of boron in both (α and β) modifications of titanium is probably less than 1 atomic percent. Previously reported values include: <0.43 At% in α and β -Ti⁽²¹⁾; <1.7 At% B at 850°C⁽²²⁾; <0.3 At% at 790°C⁽²³⁾; <0.2 At% at temperatures between 750 and 1300°C, and approximately 0.45 At% at the eutectic temperature^(9, 24). Higher solubilities found previously by P. Ehrlich⁽¹¹⁾ may be due to oxygen or nitrogen contamination of the alloys.

Phase diagram investigations of the system were carried out by A. E. Palty, et.al.⁽⁹⁾ (Figure 2). The metal-rich eutectic is formed at

Table 2. Structure and Lattice Parameters of Titanium Borides

Phase	Structure	Lattice Parameters, Å	
		Literature Values	This Investigation
Ti_2B^*	Tetragonal	$a = 6.11$ (10, 14) $b = 4.56$ $a = 6.10$ or $a = 5.24$ $c = 4.53$ or $c = 7.602$ (9)	Not confirmed
TiB^{**}	F.C.C. B_3 (13), B1	$a = 4.21$ (11) $a = 4.24$ (12) $a = 4.26$ (9)	Not confirmed
TiB	Orthorhom. B27-Type (FeB)	$a = 6.12$ $b = 3.06$ (17) $c = 4.56$	$a = 6.10 \pm 0.03$ $b = 3.06 \pm 0.01$ $c = 4.56 \pm 0.01$
TiB_2	Hexag. C32-Type	$a = 3.02$ (11) $c = 3.21$ $a = 3.028$ (19, 30, 31) $c = 3.228$	$a = 3.032$ $c = 3.225$
Ti_2B_5	Hexag. $B8_h$ -Type (W_2B_5)	$a = 2.98$ $b = 13.98$ (14, 10)	Not confirmed
$TiB_{\sim 10}$	n.d.	(20)	Not confirmed

*Previous observations probably refer to TiB (B27)

**Probably (O, N, C)-stabilized impurity phases

1640 \pm 25°C and a boron concentration of approximately 14 atomic percent.

Ti_2B forms in a peritectic reaction at 2200°C, and decomposes at approximately 1800°C into monoboride and melt. The monoboride melts incongruently at temperatures around 2000°C, while the diboride melts with a maximum at temperatures in the vicinity of 2900°C (Table 3).

Table 3. Reported Melting Temperatures for Titanium-Boron Alloys

	Temperature, °C	Composition, At% B	Investigator	Ref
Ti+TiB Eutectic	1670 \pm 25°	~ 14	A. E. Palty, et.al. (1954)	9
Ti ₂ B (dec.)	2200 \pm 50°	~ 32	A. E. Palty, et.al. (1954)	9
TiB	2060° (Peritectoid)	~ 50	A. E. Palty, et.al. (1954)	9
	1900 \pm 50°	--	P. Schwarzkopf and F. W. Glaser (1953)	25
TiB ₂	2900 \pm 80°	~TiB ₂	E.R. Honak, R. Kieffer and F. Benesovsky (1951)	26, 27
	2920°		P. Schwarzkopf and F. W. Glaser, (1953)	25
	2890°		F. W. Glaser and W. Ivanick, (1953)	28
	2920°		B. Post, et.al. (1954)	29

III. EXPERIMENTAL PROGRAM

A. SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURES

1. Starting Materials

The elemental powders as well as titanium diboride were employed for the preparation of the experimental alloy material.

Titanium metal was purchased in powder form from Var-Lac-Oid Chemical Company. It had the following impurities (contents in ppm): C-1300, H-1500, N-50, Fe-500, and Cl-200; the oxygen content was below 300 ppm. The lattice parameters of the titanium powder, obtained from a Debye-Scherrer photograph with Cu-K_α-radiation were $a = 2.94, \text{\AA}$, and $c = 4.68, \text{\AA}$, which is in good agreement with reported values of $a = 2.950 \text{\AA}$ and $c = 4.6833 \text{\AA}$ (32).

The diboride was prepared by direct combination of the elements at high temperatures. In order to circumvent difficulties arising from the violent reaction encountered in the formation of the diboride, a master alloy containing 85 atomic percent boron was initially prepared. This intermediate reaction product was then comminuted, mixed with the necessary amount of excess metal, and again reacted for 2 hrs at 1800 to 2000°C under a high purity helium atmosphere. After cooling under vacuum and discarding of the zones adjacent to the tantalum-container, the reaction lumps were crushed, and finally comminuted in hard-metal ball mill to a grain size <60 micrometers. Cobalt traces which were picked up during the grinding process were removed by acid-leaching in an 8N mixture of hydrochloric and sulfuric acid. The chemical analysis of the diboride powder gave a boron content of 65.3 ± 0.3 atomic percent, it also contained 0.088 Wt% carbon. Roentgenographically, only the diboride was detected ($a = 3.032 \text{ \AA}$, $c = 3.224 \text{ \AA}$), while the metallographic inspection revealed the presence of minute traces of excess metal phase.

2. Specimen Preparation and Heat Treatment

Altogether, a total of approximately 80 different alloy compositions were prepared for melting point, DTA, as well as X-ray studies on solid-state equilibrated samples.

Alloys with more than 55 atomic percent boron were hot-pressed, while metal-rich alloys were prepared by cold-pressing and subsequent sintering, as well as by arc-melting of the cold-compacted mixtures. Selected samples from the very metal-rich (<15 At% boron) region, specifically intended for melting point and DTA-studies, were electron-beam molten (Heraeus gun ES-2/4) under a vacuum of better than 10^{-5} Torr.

Homogenization treatments were carried out in a tungsten mesh element furnace, manufactured by the R. Brew Company. The low temperature runs were made under vacuum (120 hrs at 1250°C, $<2.10^{-5}$ Torr) whereas a second sample series was treated for 40 hrs at 1400°C under a high purity helium atmosphere. To assure maximum protection of the alloys from contamination, the tantalum sample container was wrapped in zirconium-foil. Equilibration studies at temperatures in excess of 1600°C were carried out in the Pirani melting point furnace⁽³³⁾, and the samples were quenched in a tin bath.

Approximately one-third of the total alloy material was chemically analyzed for their boron contents, and check analysis for oxygen and nitrogen were performed on selected samples. In general, the deviation from the nominal compositions were within the analytical error limits, and, as would be expected from the presence of boron, only negligible oxygen concentrations were measured in the alloys after the high temperature runs.

3. Experimental Procedures

In the following sections the experimental procedures followed in the course of the investigation are briefly discussed. Detailed descriptions of the Pirani melting point furnace, as well as the DTA-apparatus have been given in earlier reports^(33, 34), and will be repeated here only to an extent as it proves to be necessary for an understanding of the techniques followed in the experimentations.

a. Melting Point Determinations

The melting temperatures of the alloys were measured using the previously described Pirani-technique. A small sample bar, in the order of 25 mm long and with a quadratic cross section

of ~ 40 mm² is heated resistively to the temperature of the phase change. The temperature of the sample is measured optically with a disappearing-filament type micropyrometer through a quartz window in the furnace wall. A small hole, generally in the order of 0.6 mm in diameter, drilled or pressed into the sample, serves as the reference point for the measurements. The consistency (precision) of the measurements with the Pirani-technique is usually better than $\pm 4^\circ\text{C}$ at 2000°C and $\pm 10^\circ\text{C}$ at 3500°C for homogeneously melting alloys; it is lower on two-phased melting specimens, where the attainable accuracy also depends on the compositions of the phases formed during melting.

The overall uncertainties in the temperature are composed of two parts: The precision of the measurements, and the errors in the pyrometer calibrations. They can be computed from the relation

$$\bar{\sigma} = \pm \sqrt{\sigma_c^2 + \sigma_m^2}$$

where $\bar{\sigma}$ stands for the overall temperature uncertainty, σ_c for the standard deviation in the pyrometer calibration in the given temperature range, and σ_m denoting the precision of the measurement. Typical calibration uncertainties are $\pm 10^\circ\text{C}$ at 2300°C , $\sim \pm 17^\circ\text{C}$ at 3000°C , and $\pm 30^\circ\text{C}$ (estimated) at 4000°C .

The relative accuracy of the experimental data is best indicated by the precision of the measurements; hence, unless otherwise specified, the temperature figures presented in the text or on the phase diagram drawings refer to the precision of the measurements, and do not include the calibration error.

b. Differential Thermal Analysis

The measurements were carried out under a high purity helium atmosphere of 2.5 atmospheres, using graphite as reference material. To retard interaction between the sample and the graphite containers, linings consisting of tantalum as well as of the diborides of titanium, zirconium, and hafnium, were employed. In view of the container problem, the investigations had to be limited to temperatures below 2500°C.

c. X-Ray Analysis

Since the crystal structures of all phases were known, only powder patterns in the Cu-K_α -radiation were prepared. Excessive fluorescent radiation from titanium-containing alloys, causing heavy background blackening, was eliminated by absorption in a cover film.

The exposures were made in a 57.4 mm dia camera on a Siemens Crystalloflex II unit, and the films were measured on a Siemens Kirem coincidence scale with precision micrometer attachment.

d. Chemical Analysis

The principle of the wet-chemical method used for the determination of boron consists in converting the boron (free or bound) to boric acid, which then is determined by differential titration of the complex acid formed with mannitol.

In brief, the procedures were as follows: The powdered metal-boron alloys were fused at 1000°C in pre-dried sodium carbonate and the resulting melt-cake dissolved in water. Excess carbonate was precipitated with barium hydroxide, and was, together with other hydroxide precipitates, removed by filtration. The resulting filtrate was then acidified to a pH value of 5.3 and, after addition of mannitol, titrated

differentially with N/10 NaOH between pH 5.3 and 8.5. The consistency of the data obtained with this method varied somewhat with the boron content, but was generally within the limits of ± 0.3 atomic percent.

The carbon content of the alloys was analyzed by using the standard combustion technique. For low carbon contents (< 0.1 Wt%), the oxygen, nitrogen, and hydrogen were determined by the gas-fusion technique, and small impurity contents were determined in a semiquantitative way spectrographically.

e. Metallographic Procedures

The specimens were mounted in an electrically conductive combination of diallyl-phtalate and lucite-coated copper powder, and coarse-ground on silicon carbide papers having grit sizes between 120 and 600. A slurry of 0.3 micrometer alumina powder and Murakami's solution was employed for final polishing.

Electrolytic anodizing in 2% NaOH proved to be a very effective means for positive phase distinction in excess metal containing alloys, and also for the development of the microstructures in single phased diboride samples. The phase contrasts in excess boron alloys were sufficiently high to permit an examination in the as-polished state. Etching in a 10% solution of Aqua Regia and hydrofluoric acid occasionally was employed for the development of structural details in two-phases mono- and diboride samples.

The etching procedures are summarized in Table 4.

Table 4. Etching Procedures for Titanium-Boron Alloys*

Alloys	Etching
0-57 At% B	Anodizing in 2% NaOH
57-64 At% B	Anodizing in 2% NaOH or etching in 10% Aqua Regia + Hf
65-68 At% B	Anodizing in 2% NaOH
>69 At% B	No etching required

*Appearance of the individual phases after electroetch:

Ti: Light blue

TiB: Light brown

TiB₂: Bright (appearance essentially unchanged)

B. RESULTS

1. The Titanium Phase

Eight melting point measurements, performed on cold-pressed as well as electron-beam molten titanium⁽⁵¹⁾, gave an average melting temperature of $1668 \pm 4^\circ\text{C}$; taking into account the pyrometer calibration error, the overall temperature uncertainty becomes $\pm 8^\circ\text{C}$.

The boron solubility at 1540°C in titanium is less than one atomic percent (Figure 3) and the α - β -transformation temperature remains practically unchanged (Figures 4 and 5). Although not conclusive, the appearance of the microstructures of low boron alloys suggests a peritectoid reaction, according to



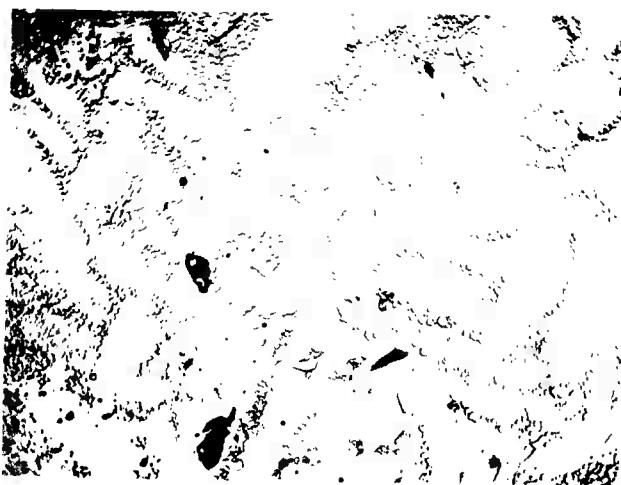


Figure 3. Ti-B (1 At% B), Quenched with 70°C per Second from 1550°C. X1250
β-Ti (Transformed), and Traces of Excess Monoboride.

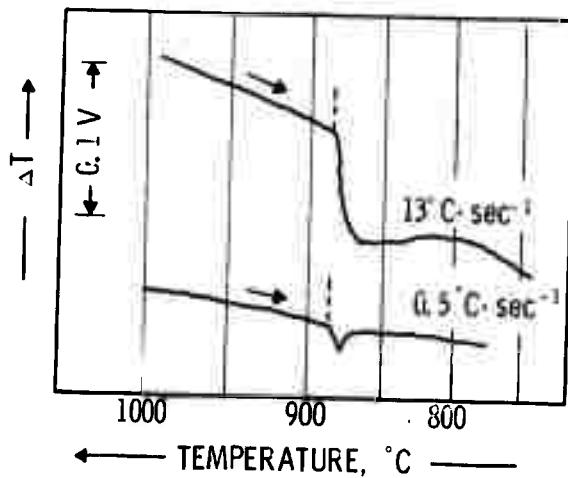


Figure 4. DTA-Thermograms (Cooling) of Crystal-Bar Titanium

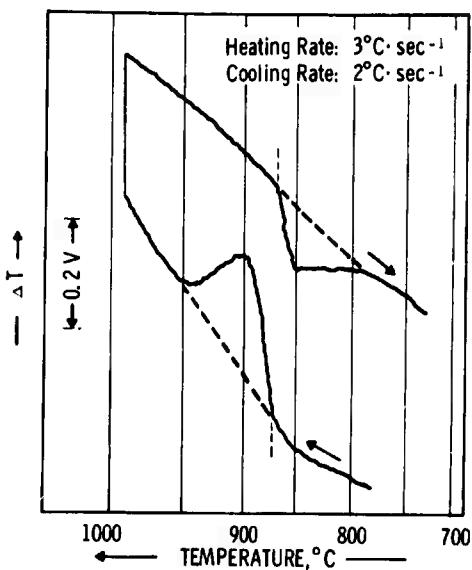


Figure 5. DTA-Thermogram of a Titanium-Boron Alloy with 6 Atomic Percent Boron.

2. The Concentration Range Ti-TiB₂

Upon addition of small amounts of boron to titanium, the measured melting temperatures drop rapidly from 1668°C, the melting point of titanium, to ~1540°C, the reaction isotherm of the Ti + TiB eutectic (Table 5). Alloys from the concentration range 5 to 44 atomic percent boron are two-phased after quenching from temperatures below 2200°C, containing α -Ti and TiB. In the average, lattice parameters of $a = 2.95 \text{ \AA}$, and $c = 4.449 \text{ \AA}$ were measured for the α -titanium (transformed β -Ti) phase in excess monoboride-containing alloys. This nominal change of the lattice dimensions as compared to pure α -titanium ($a = 2.949 \text{ \AA}$, $c = 4.688 \text{ \AA}$) suggests a very small boron solubility only; this finding is in essential agreement with the metallographic results (Figure 3).

Table 5. Melting Temperatures of Titanium-Boron Alloys and Qualitative Phase Evaluation

No.	Nom. Anal.	Melting Temperatures		Melting	Phases	X-Ray Lattice Parameters, Å	Metallography
		At% Boron	Incipient Collapse				
1	0	n. d.	1663+4°	1668+4°	Sharp	n. d.	Single Phase Ti
2	5	4.3	1540°	1548°	Sl. Heterog	n. d.	Ti+(Ti+TiB) Eutectic
3	10	n. d.	1542°	1545°	Sharp	Ti + TiB	Ti+(Ti+TiB) Eutectic
4	15	16.1	1535°	1541°	Sl. Heterog	Ti + TiB	Ti:a=2.95 ₁ ; c=4.69 ₀ Å
5	20	n. d.	1542°	1548°	Heterog	Ti + TiB	Ti:a=2.95 ₁ ; b=4.69 ₁ Å
6	23	22.8	1535°	1544°	Heterog	Ti + TiB	Ti:a=2.95 ₁ ; b=4.69 ₁ Å
7	26	27.5	1543°	1546°	Heterog	Ti + TiB	n. d.
8	29	n. d.	1538°	1549°	Heterog	Ti + TiB	n. d.
9	32	n. d.	1539°	1561°	Heterog	Ti + TiB	n. d.
10	35	n. d.	1560°	1565°	Very Heterog	Ti + TiB	n. d.
11	38	n. d.	1540°	1555°	Very Heterog	Ti + TiB	n. d.
12	41	n. d.	1565°	1633°	Very Heterog	Ti + TiB	n. d.
13	44	44.6	1545°	1945°	Very Heterog	Ti + TiB	TiB:a=6.11Å; b=3.07Å; c=4.56Å
14	46	n. d.	1582°	2230°	Heterog	Ti+TiB+TiB ₂	TiB:a=6.16Å; b=3.06Å; c=4.56Å
15	48	48.4	2196°	2322°	Heterog	Ti+TiB+TiB ₂	n. d.
16	50	50.2	2200°	2302°	Heterog	Ti+TiB+TiB ₂	Ti + TiB + TiB ₂
17	52	52.2	2224°	2300°	Heterog	TiB+TiB+TiB ₂	Ti + TiB + TiB ₂
18	54	n. d.	2218°	2258°	Heterog	TiB ₂ + TiB ₂	n. d.
19	55	n. d.	2206°	2486°	Very Heterog	TiB + TiB ₂	TiB:a=6.12Å; b=3.06Å; c=4.55Å
20	58	n. d.	2199°	2800°	Very Heterog	TiB+TiB ₂ +Ti	n. d.
21	60	n. d.	2240°	n. d.	Very Heterog	TiB + TiB ₂	n. d.

Table 5 (Continued)

No.	Nom. Anal.	At% Boron	Melting Temperatures °C	Incipient Collapse	Melting	Phases	X-Ray		Metallurgy
							Lattice Parameters, Å	Lattice Parameters, Å	
22	62	n. d.	2310*	3188*	Very Heterog	TiB + TiB ₂	n. d.	TiB + TiB ₂	
23	64	64.4	2743*	3178*	Very Heterog	TiB ₂ +Trace TiB	TiB ₂ ;a=3.032Å;c=3.224Å	Ti+TiB ₂ +Trace TiB	
24	65	65.2	3160+30*	3160+30*	Fairly Sharp	TiB ₂	TiB ₂ ;a=3.032Å;c=3.225Å	TiB ₂ +Trace Ti	
25	65.5	65.2	3190+20*	3190+20*	Sharp	TiB ₂	n. d.	TiB ₂ +Trace Ti	
26	65(4)	66.0	3225+20*	3225+20*	Sharp	TiB ₂	TiB ₂ ;a=3.032Å;c=3.224Å	TiB ₂	
27	66.5	66.3	3198+25*	3198+25*	Sharp	TiB ₂	TiB ₂ ;a=3.032Å;c=3.225Å	TiB ₂ +Trace B	
28	67(4)	66.8	3178+20*	3178+20*	Sharp	TiB ₂	TiB ₂ ;a=3.032Å;c=3.225Å	TiB ₂ +Trace B	
29	68(4)	67.4	3165+30*	3165+30*	Fairly Sharp	TiB ₂	n. d.	TiB ₂ +B	
30	59	68.5	2100*	3060*	Very Heterog	TiB ₂	n. d.	TiB ₂ +B	
31	70	70.0	2115*	2635*	Very Heterog	TiB ₂	TiB ₂ ;a=3.031Å;c=3.225Å	n. d.	
32	72	n. d.	2120*	2615*	Very Heterog	n. d.	n. d.	n. d.	
33	74	n. d.	2130*	2605*	Very Heterog	n. d.	n. d.	n. d.	
34	77	n. d.	2094*	2330*	Very Heterog	n. d.	n. d.	TiB ₂ +B	
35	80	n. d.	2100*	2330*	Very Heterog	n. d.	n. d.	TiB ₂ +B	
36	84	n. d.	2112*	2270*	Very Heterog	TiB ₂	TiB ₂ ;a=3.032Å;c=3.224Å	TiB ₂ +B	
	88	n. d.	n. d.	n. d.	n. d.	TiB ₂	TiB ₂ +B	TiB ₂ +B	

For the metallographic location of the Ti + TiB eutectic (Figures 6 through 9), rapid quenching of the alloys from above solidus proved to be essential, since the TiB grains present in the eutectic structure segregate extremely rapid grain boundaries, thus simulating the presence of 'primary' crystallized titanium (Figure 9).

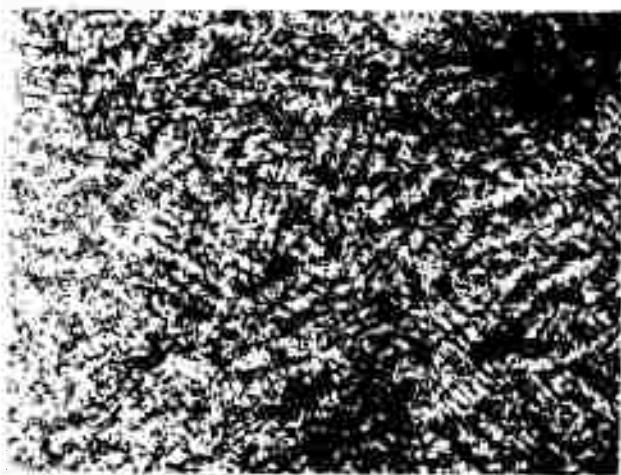


Figure 6. Ti-B (4.3 At% B), Quenched with $\sim 100^{\circ}\text{C}$ per Second from 1550°C . X100

Primary β -Ti (Transformed), in a Matrix of Ti + TiB Eutectic.

Hypereutectic compositions melt increasingly heterogeneously as the boron concentration approaches the compositions of the monoboride (Figure 10). Incipient melting rises to 2190°C in the equiatomic concentration region, but melting of the alloys always remains



Figure 7. Enlarged View of the Sample Shown in Figure 6 X500



Figure 8. Ti-B (7.2 At% B), Quenched with ~300°C per Second from 1550°C. X350

Ti + TiB Eutectic

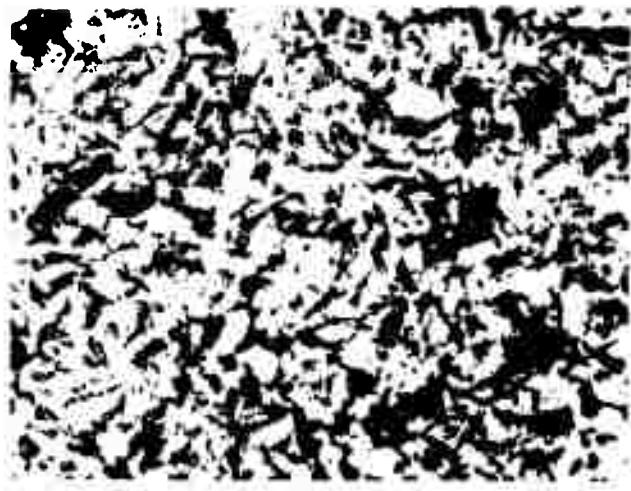


Figure 9. Ti-B (10 At% B), Cooled with $\sim 30^\circ\text{C}$ per Second from 1550°C . X500

Primary TiB (Large, Dark Crystals) in Partially Segregated Ti + TiB Eutectic.

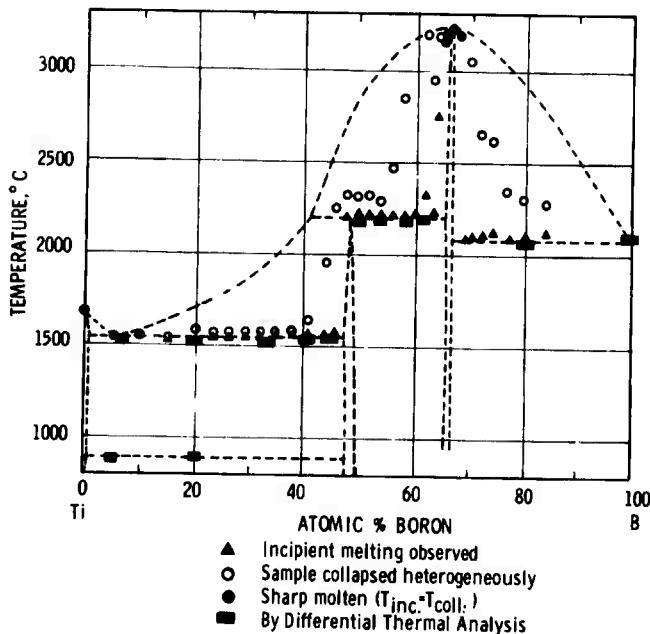


Figure 10. Melting Temperatures and Solid State Reaction Isotherms in the Titanium-Boron System.

two-phased (incongruent). The composition of the peritectic was bracketed to 42 ± 3 atomic percent boron by metallographic examination of samples which were cooled from temperatures slightly above the peritectic (Figure 11). Although the structure closely resembles that of a eutectic reaction, inspection of the micrographs at magnifications up to 2500 revealed the monoboride as a secondary product formed by reaction between the metal and the diboride phase.

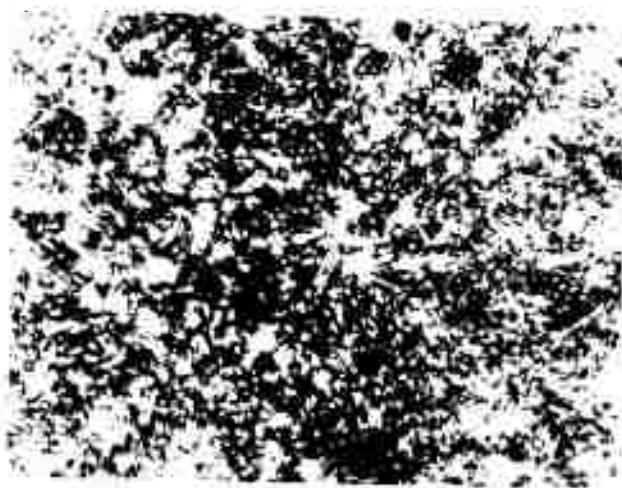


Figure 11. Ti-B (42 At% B), Cooled with $\sim 30^\circ\text{C}$ per Second from 2210°C . X1000

Peritectic: $\text{Ti} + \text{TiB}$

X-Ray: $\text{Ti} + \text{TiB}$

Alloys with boron concentrations slightly less than 50 atomic percent and which were slowly cooled from temperatures not exceeding 2180°C consist of titanium and titanium monoboride (Figure 12), whereas the peritectic reaction becomes clearly recognizable, once the peritectic temperature was exceeded in the experiments (Figure 13 and 14).



Figure 12. Ti-B (40 At% B), Cooled with 3°C per Second from 2140°C. X1000
Ti (Light), and TiB Crystals (Dark).

In this connection it is interesting to note the different etching behavior of the monoboride phase, depending, whether it had formed in the initial peritectic reaction between melt and diboride, or during the bivariant solidification reaction between peritectic and eutectic line. The more rapid etchant attack on the lower-temperature formed monoboride possibly may be related

to imperfections in the link-up of the crystals formed by physical segregation and partial collective recrystallization during cooling.



Figure 13. Ti-B (50 At% B), Cooled with 0.5°C per Second X500
from 2210°C.

Peritectic Reaction Mixture $Ti + TiB + TiB_2$
Light Grains Within Slightly Shaded Matrix:² Unreacted TiB_2
Dark Grains: TiB Formed During Bivariant Solidification
Between 2190° and 1540°
Bright Grains, Surrounded by TiB (Dark): Ti

The sequence of reactions in the concentration range from 0 to 60 atomic percent boron were independently studied by differential thermal analysis (Figures 15 and 16); the results are in general confirmation the data obtained primarily by the other techniques employed in the investigations.



Figure 14. Ti-B (48 At% B), Cooled with 0.5°C per Second from 2200° to 2160°, Held for 2 hrs at 2160°C, and Cooled with 0.5°C per Second to Room Temperature.

X1000

Light (Actual Etching Color Blue): Rest Amounts of Ti
Shaded: TiB, Formed by Reaction Between Melt and Diboride
Dark: TiB, Formed During Bivariant Solidification Between
2160° and 1540°
X-Ray: TiB

Alloys with boron concentration between ~50 and 66 atomic percent boron, and which were annealed at temperatures below 2200°C are two-phased, containing TiB and TiB_2 in varying amounts (Figure 17); samples quenched from above 2200°C show primarily diboride and metal, i.e. the peritectic reaction becomes suppressed at higher cooling speeds.

No homogeneity range of any significance could be detected for the monoboride and the lattice parameters were practically identical in excess metal or excess diboride containing alloys. The parameters

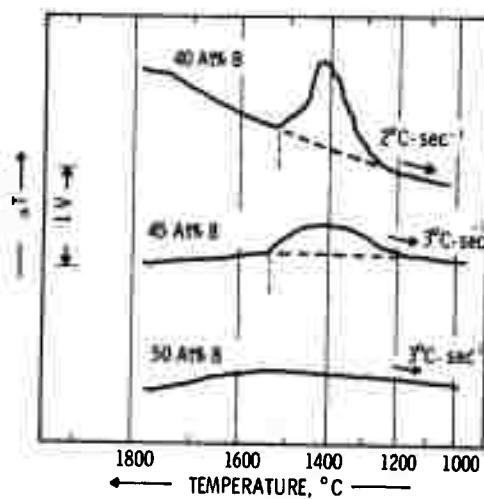


Figure 15. DTA-Thermograms (Cooling) of Titanium-Boron Alloys from the Concentration Range Ti-TiB.

Note Absence of the Eutectic Reaction in the Alloy with 50 Atomic Percent Boron.

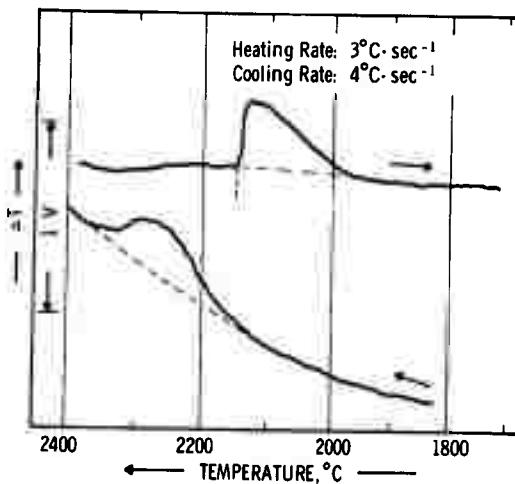
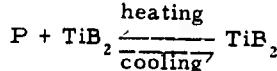


Figure 16. DTA-Thermogram of a Titanium-Boron Alloy with 58 Atomic Percent Boron, Showing the Peritectic Reaction:



at Temperatures Between 2100 and 2200°C.

found by us are identical to those determined in the original structure determination by B. F. Decker and J. S. Kasper⁽¹⁷⁾ (Table 2).

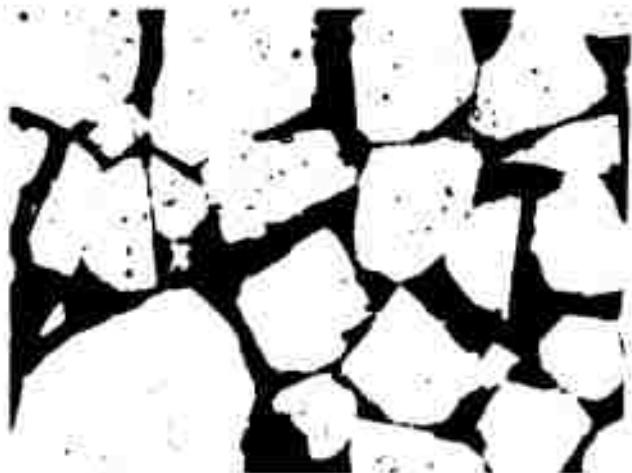


Figure 17. Ti-B (58 At% B), Melted, and Reannealed for 2 Hours at 2000°C. X1000

TiB₂ (Light), Surrounded by Dark Crystals of TiB.

3. The Diboride Phase and Boron-Rich Equilibria

The melting temperatures of the alloys show a sharp increase as the stoichiometric composition is approached (Table 5); congruent melting was found to occur at a temperature of 3225°C and a boron concentration of approximately 66 atomic percent. The first appearance of excess boron in the melting experiments was noticed in the sample having 68.5 atomic percent boron, where it tended to exude from the sample at temperatures in the vicinity of 2100°C.

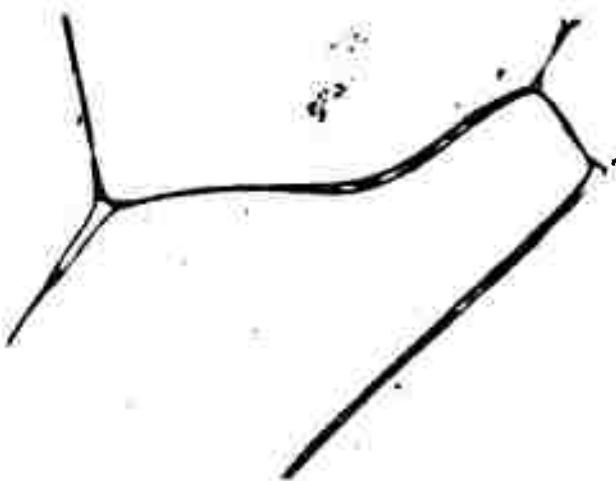


Figure 18. TiB (64.4 At% B), Quenched from 2400°C. X1000

TiB₂ with Small Quantities of Ti and TiB at the Grain Boundaries.

X-Ray: TiB₂ + Traces TiB.

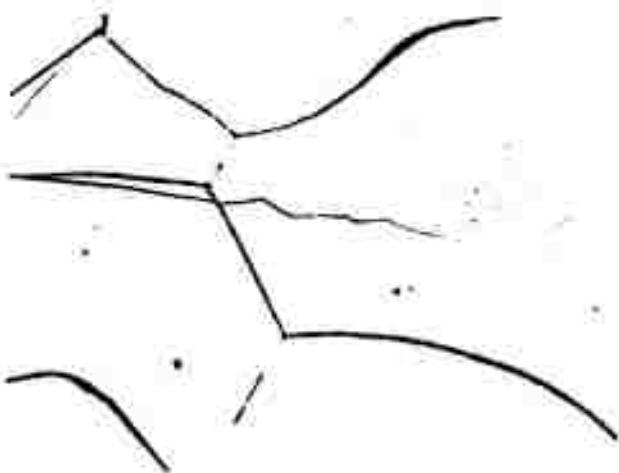


Figure 19. Ti-B (65.2 At% B), Quenched from 2600°C. X800

TiB₂ with Traces of Ti and TiB at the Grain Boundaries

X-Ray: TiB₂

The homogeneity range of the diboride phase is probably below 2 atomic percent over the entire solidus range. Alloys with analyzed boron contents of 64.4 and 65.2 atomic percent still contain small quantities of excess metal or monoboride at the grain boundaries (Figures 18 and 19). A sample with 66 At% B is metallographically single phase (Figure 20), while alloys with 66.3 and 66.8 At% B, prepared under similar conditions, already show increasing amounts of free boron at the grain boundaries (Figures 21 and 22). No further higher-boron phase could be detected

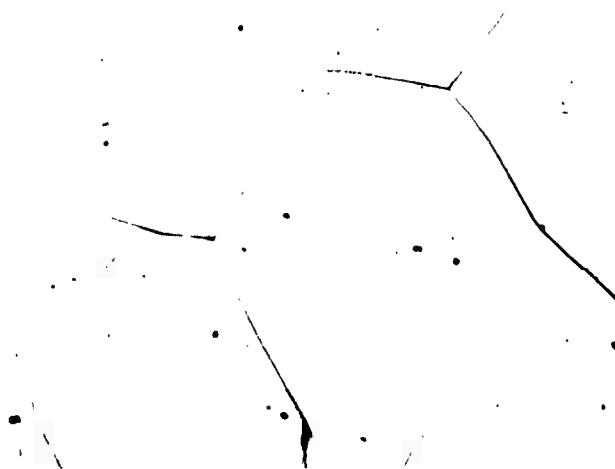


Figure 20. Ti-B (66 At% B), Quenched from 2900°C.

X550

Single Phase TiB_2

either metallographically or by X-ray; instead, the relative amount of free boron, easily recognizable on its dull grey appearance, increases steadily with increasing boron content of the alloys.



Figure 21. Ti-B (60.3 to 66.5 At% B), Quenched from ~ 3000°C. X1500

TiB_2 with Cracks, and Scant Traces of Grain Boundary Boron.



Figure 22. Ti-B (66.8 At% B), Quenched from ~ 3000°C. X1500

TiB_2 with Excess Boron at the Grain Boundaries.

The small homogeneity range of the diboride found by metallography was also verified by X-ray diffraction, which showed the lattice dimensions of TiB_2 to be practically independent of the boron content of the alloys (Table 5).

The boron-rich eutectic reaction isotherm, located by melting point (Figure 10) as well as by DTA measurements (Figure 23), occurs at 2080°C. Although not specifically investigated, the eutectic point must be located close to boron, since arc melted samples with nominal boron contents of 90 and 95 atomic percent already contained significant amounts of primary crystallized diboride, and the boron matrix contained minute quantities of TiB_2 only.

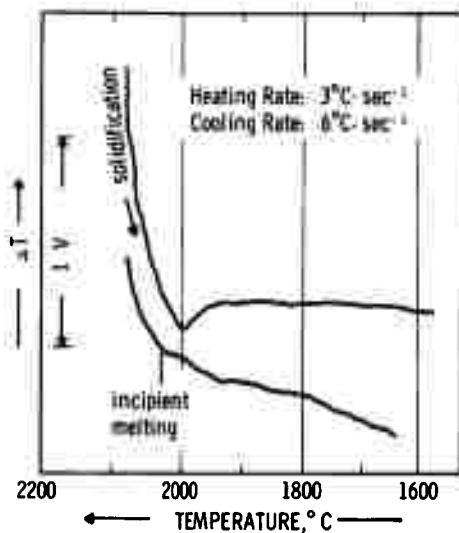


Figure 23. DTA-Thermogram of a Titanium-Boron Alloy with 80 Atomic Percent Boron.

IV. DISCUSSION

A comparison of the present diagram with the literature data (Figure 2) indicates a melting temperature for the diboride phase, which is approximately 300°C higher than previous measurements (Table 3). The reasons for these discrepancies are difficult to assess, since in neither instance were the methods used in the experimentations adequately described. If one assumes, however, that in the investigations of F. W. Glaser, et.al. (25, 28, 29) the measurements were carried out in graphite containers as they describe it for the zirconium-boron system⁽³⁵⁾, the observed melting temperatures would correspond to temperatures somewhere between the true melting point of TiB_2 and that of the TiB_2 -C eutectic.

For the metal-rich eutectic isotherm we find a temperature which is approximately 130°C lower than that reported by A. E. Palty, et.al. (9). No signs for the existence of a compound Ti_2B could be detected in the present investigations; instead, the alloys with boron concentrations up to 50 atomic percent are two-phased Ti and TiB . These findings, as well as the fact, that the peritectic temperature for Ti_2B measured by A.E. Palty, et.al. (Figure 2) practically coincides with our value for TiB , tend to confirm B. Aronsson's⁽¹⁵⁾ opinion, that previous observations of a compound Ti_2B actually referred to the orthorhombic monoboride, discovered later by B.F. Decker and J. S. Kasper⁽¹⁷⁾. We also were unable to prepare a Ti_2B_5 phase such as described by B. Post and F.W. Glaser⁽¹⁰⁾, or a $TiB_{\sim 10}$ found by H. M. Greenhouse, et.al.⁽²⁰⁾.

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13 ABSTRACT

The binary system Ti-B, has been investigated by means of X-ray, metallographic, melting point, and differential thermoanalytical techniques, and a complete phase diagram for the system was established. The results of the present investigation are discussed and compared with previous findings.

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